LOCAL THEORY OF ELECTRONIC STRUCTURE OF EXTENDED SYSTEMS

by Walter Kohn and Avishay Yaniv

ABSTRACT

We present a theory of local electronic structure that yields the local density of states $n(\mathbf{r},E)$ and related quantities. The theory applies whether the electronic wave functions themselves are delocalized or not and requires a knowledge of the Hamiltonian only in the vicinity of $\mathbf{r}$. Several simple examples are worked out with good results. Possible applications include periodic and non-periodic transition metal systems and large molecules.

I. INTRODUCTION

One of the most general characteristics of condensed matter, in its normal state, is that the electronic properties in the vicinity of a point $\mathbf{r}$ depend significantly on the electrostatic potential $\phi(\mathbf{r}')$ at points $\mathbf{r}'$ near $\mathbf{r}$. This physical property of "locality" is not directly evident from the wave-mechanical equations that govern such a system. Thus, for example, in the framework of the density functional theory, one is required to solve the wave equations

$$(-\tfrac{1}{2}\nabla^2 + V(\mathbf{r}))\ \psi^\nu(\mathbf{r}) = E^\nu\psi^\nu(\mathbf{r}) \quad , \tag{1.1}$$

where $V(\mathbf{r})$ is an appropriately calculated effective potential. A typical physical property, such as the local single-particle density of states, averaged over a finite energy interval ΔE, is given by a sum over states

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$$\bar{n}(\mathbf{r},E) = \frac{1}{\Delta E} \sum_{E<E^{\nu}<E+\Delta E} |\psi^{\nu}(\mathbf{r})|^2 \quad . \tag{1.2}$$

The individual normalized eigenfunctions $\psi^{\nu}(\mathbf{r})$ are in general not localized, and do not have the locality property mentioned above; i.e., their value at a point $\mathbf{r}$ is, in general, strongly sensitive to changes in $V(\mathbf{r}')$ even for $\mathbf{r}'$ arbitrarily far from $\mathbf{r}$. However, physical quantities involving sums, such as in Eq. (1.2), have been found in practice to have the locality property. As a simple example we mention that calculated physical properties of a solid surface are substantially the same whether one calculates them for a semi-infinite solid or a slab a few layers thick.

In recent years several calculational techniques have been developed and applied, which depend on this locality property. Among these we mention cluster[1,2,3,4] calculations, in which an extensive system is replaced by a small cluster of atoms surrounding the point of interest; and moments (and related) methods[5,6] used in conjunction with the tight binding approximation for the eigenfunctions $\psi^{\nu}(\mathbf{r})$.

In a recent paper[7] we have proved a strict locality theorem for the Laplace transform of the local density of states (LDS)

$$\varrho(\mathbf{r},\beta) \equiv \int n(\mathbf{r},E)\, e^{-\beta E} dE \quad , \tag{1.3}$$

which we call the local partition function (LPF). We proved that if the potential $V(\mathbf{r}')$ was changed only at distant points $\mathbf{r}'$, with $|x_i'-x_i|>a$, the effect on $\varrho(\mathbf{r},\beta)$ decayed in a Gaussian fashion as a function of a. A similar result was also proved for the more general density matrix $\varrho(\mathbf{r},\mathbf{r}';\beta)$, which reduces to $\varrho(\mathbf{r},\beta)$ for $\mathbf{r}=\mathbf{r}'$.

This suggests that $\varrho(\mathbf{r},\mathbf{r}';\beta)$ and $\varrho(\mathbf{r},\beta)$ could be approximately calculated in a basis of functions, $u_n(\mathbf{r}'')$, localized near the points $\mathbf{r}$ and $\mathbf{r}'$ under consideration, whether the eigenfunctions, $\psi^{\nu}(\mathbf{r})$, are localized or extended. This will indeed be shown to be possible. The mechanics of the method is similar to the Rayleigh-Ritz method for a finite system. However, except in special cases, it does not yield approximate eigenfunctions. It does yield an arbitrarily close approximation to local physical quantities, such as $\varrho(\mathbf{r},\mathbf{r}';\beta)$ or $\bar{n}(\mathbf{r},E)$.

We shall also point out how this direct method of locally calculating $\bar{n}(\mathbf{r},E)$ (without having to calculate the extended eigenfunctions of the entire extended system) can be used in conjunction with the density functional theory.[8,9] In this way, many-body effects can be incorporated, and quantities such as the density $n(\mathbf{r})$ and the energy density $e(\mathbf{r})$ of extensive systems can be calculated self-consistently. Since, in view of general density

functional theorems, all physical properties are functionals of $n(\mathbf{r})$, other quantities—like the many-body density of states, etc.—can in principle be subsequently obtained.

Finally, we report several illustrative examples, free electrons, electrons at interfaces, and hybridized electrons, which demonstrate how the method works in practice.

II. THE BLOCH EQUATION OF MOTION IN A LOCALIZED REPRESENTATION

Clearly, the density matrix $\varrho(\mathbf{r}_1,\mathbf{r}_2;\beta)$ satisfies the so-called Bloch equation of motion

$$\frac{\partial}{\partial\beta}\varrho(\mathbf{r}_1,\mathbf{r}_2;\beta) = -H(\mathbf{r}_2)\,\varrho(\mathbf{r}_1,\mathbf{r}_2;\beta) \tag{2.1}$$

and the initial condition

$$\varrho(\mathbf{r}_1,\mathbf{r}_2;0) = \delta(\mathbf{r}_1-\mathbf{r}_2) \quad . \tag{2.2}$$

For a first orientation, we consider the case of free electrons $H(\mathbf{r}_2) = -\tfrac{1}{2}\nabla_2^2$. Eq. (2.1) becomes

$$\frac{\partial}{\partial\beta}\varrho_o(\mathbf{r}_1,\mathbf{r}_2;\beta) = \tfrac{1}{2}\nabla_2^2\,\varrho_o(\mathbf{r}_1,\mathbf{r}_2;\beta) \quad . \tag{2.3}$$

This is the equation for heat-conduction if β is interpreted as time and ϱ_o as the temperature at $\mathbf{r}_2$, $\mathbf{r}_1$ being an idle parameter. In this case (2.1) and (2.2) represent the heat flow from an initial point source. The solution is given by a spreading Gaussian

$$\varrho_o(\mathbf{r}_1,\mathbf{r}_2;\beta) = \frac{1}{(2\pi\beta)^{3/2}}\exp(-|\mathbf{r}_2-\mathbf{r}_1|^2/2\beta) \quad . \tag{2.4}$$

When the Hamiltonian contains also a potential energy, $V(\mathbf{r})$, the behavior of ϱ for short times, β, is still given by (2.4), since the effect of the kinetic energy operator $\tfrac{1}{2}\,p^2$ is much greater than $V(\mathbf{r})$ in view of the very short wavelength of the Fourier components of ϱ. At longer times, the Bloch equation (2.1) may be regarded as a modified heat diffusion equation. The solution is a wave-packet (in $\mathbf{r}_2$) spreading out from the original point source at $\mathbf{r}_1$.

Suppose we are interested in $\varrho(\mathbf{r}_1,\mathbf{r}_2;\beta)$ for $\mathbf{r}_1$ and $\mathbf{r}_2$ near the origin. Then, in view of the character of ϱ described above, we may expand it in a complete set of functions, u_n, localized near the origin,

$$\varrho(\mathbf{r}_1,\mathbf{r}_2;\beta) = (\mathbf{r}_1|e^{-\beta H}|\mathbf{r}_2) =$$

$$\lim_{N\to\infty} \sum_{n_1,n_2=1}^{N} (\mathbf{r}_1|n_1)(n_1|e^{-\beta H}|n_2)(n_2|\mathbf{r}_2). \tag{2.5}$$

In practice, the sums will have to be terminated at a finite value of N. Let k_N be a typical wave-number in the Fourier transform of u_N. Then, since the characteristic wave-number of the *short* time solution $\varrho_o(\mathbf{r}_1,\mathbf{r}_2;\beta)$ is $\beta^{-1/2}$, an adequate expansion for a short time β requires N to be large enough so that

$$k_N \geq \beta^{-1/2} \qquad \text{(for small } \beta\text{)} \quad . \tag{2.6}$$

For *long* times β, we see from the free electron example, Eq. (2.4), that the solution spreads out. Let us denote its spatial dimension by $R(\beta)$ (for free electrons, $R_o(\beta) \sim \sqrt{2\beta}$). Then, if the range of u_N is denoted by R_N, an adequate expansion of ϱ requires

$$R_N \geq R(\beta) \qquad \text{(for large } \beta\text{)} \quad . \tag{2.7}$$

Thus, we see that, for a fixed maximum N and corresponding values of k_N and R_N, the representation (2.5) will fail for both very small and very large β, when the conditions (2.6) and (2.7) cease to be satisfied. However, for intermediate values of β, the expansion (2.5), up to a finite large N, will be satisfactory.

Here we also note that the choice of the length scale a of the functions u_n is at our disposal. Clearly

$$k_N \propto a^{-1}, \; R_N \propto a \quad . \tag{2.8}$$

Thus, for a given N, one can choose a so as to obtain a better representation of ϱ for either small β (choose a small) or large β (choose a large).

The representation (2.5) of ϱ is inconvenient because of the appearance of the operator H in the exponential. To obtain a practical form for ϱ, we write

$$H = H_N + \Delta H_N \quad , \tag{2.9}$$

where H_N is the projection of H on the N functions u_n,

$$H_N \equiv \sum_{n_1,n_2=1}^{N} |n_1)(n_1|H|n_2)(n_2| \quad . \tag{2.10}$$

Clearly, if N functions $\{u_n\}$ are adequate for a description of ϱ, the projected operator, H_n, will be an adequate representation of H. Thus, we may replace Eq. (2.5) by:

$$\varrho_N(\mathbf{r}_1,\mathbf{r}_2;\beta) = \sum_{n_1,n_2=1}^{N} (\mathbf{r}_1|n_1)\,(n_1|e^{-\beta H_N}|n_2)\,(n_2|\mathbf{r}_2) \quad . \tag{2.11}$$

This can be transformed into a more convenient expression by diagonalizing H_N,

$$\sum_{n_2=1}^{N} (n_1|H|n_2)\,c_{n_2}^{\nu} = E^{\nu} c_{n_1}^{\nu} \tag{2.12}$$

with eigenvectors

$$\phi^{\nu}(\mathbf{r}) = \sum_{n=1}^{N} c_n^{\nu} u_n(\mathbf{r}) \quad . \tag{2.13}$$

Then, because of the fact that the $\{\phi^{\nu}\}$ arise from the $\{u_n\}$ by a unitary transformation, we can rewrite Eq. (2.11) as:

$$\varrho_N(\mathbf{r}_1,\mathbf{r}_2;\beta) = \sum_{\mu_1\mu_2=1}^{N} (\mathbf{r}_1|\mu_1)\,(\mu_1|e^{-\beta H_N}|\mu_2)\,(\mu_2|\mathbf{r}_2)$$

$$= \sum_{\mu=1}^{N} \phi^{\mu}(\mathbf{r}_1)^*\phi^{\mu}(\mathbf{r}_2)e^{-\beta E^{\mu}} \quad . \tag{2.14}$$

This is the approximate representation of ϱ in terms of the u_n's.

III. THE DENSITY MATRIX AND THE DENSITY OF STATES AS A FUNCTION OF E

From Eq. (2.14) we can immediately obtain, by Laplace inversion, an approximation to the density matrix for a given energy E,

$$n_N(\mathbf{r}_1,\mathbf{r}_2;E) = \sum_{\mu=1}^{N} \phi^{\mu}(\mathbf{r}_1)^*\,\phi^{\mu}(\mathbf{r}_2)\,\delta(E-E^{\mu}) \quad , \tag{3.1}$$

and, in particular, the local density of states

$$n_N(\mathbf{r},E) = n_N(\mathbf{r},\mathbf{r};E) = \sum_{\mu=1}^{N} |\phi^\mu(\mathbf{r})|^2 \delta(E-E^\mu) \quad . \tag{3.2}$$

We note that, in this procedure, $n_N(\mathbf{r},E)$ is a sum of δ-functions in E, even when the real density of states $n(\mathbf{r},E)$ is continuous. A well known way of smoothing (3.2) is to calculate the integrated function

$$\begin{aligned} \mathfrak{N}_N(\mathbf{r},E) &= \int^E n_N(\mathbf{r},E')dE' \\ &= \sum_{E^\mu \le E} |\phi^\mu(\mathbf{r})|^2 \quad , \end{aligned} \tag{3.3}$$

which is a stepwise monotonically increasing function of E, smooth this function to yield $\overline{\mathfrak{N}}_N(\mathbf{r},E)$, and then obtain the smoothed $\overline{n}_N(\mathbf{r},E)$ by differentiation with respect to E.

IV. FREE ELECTRONS IN A LOCALIZED REPRESENTATION

In this section we shall discuss the approximate representation of the density matrix $n(x,x';E)$, of a one-dimensional free electron gas in a basis of a finite number of harmonic oscillator functions.

The free electron Hamiltonian is

$$H_o = \tfrac{1}{2} p^2 \quad . \tag{4.1}$$

The local density of states is, in this case, independent of the position x,

$$n(x,E) = n(E) = \frac{1}{\pi} (2E)^{-\frac{1}{2}} \quad , \tag{4.2}$$

and the corresponding integrated density of states is

$$\mathfrak{N}(x,E) = \mathfrak{N}(E) = \frac{1}{\pi} (2E)^{\frac{1}{2}} \quad . \tag{4.3}$$

To calculate $n(x,E)$ at the origin, we use as basis functions the well known eigenfunctions u_n of the harmonic oscillator Hamiltonian,

$$H = \tfrac{1}{2} p^2 + \tfrac{1}{2}\omega^2 x^2 \quad , \tag{4.4}$$

with eigenvalues

$$E_n = \omega(n + \tfrac{1}{2}) \quad . \tag{4.5}$$

In this representation the matrix elements of H_o are

$$(m|H_o|n) = \frac{\omega}{4}\left[-\sqrt{(n-1)n}\,\delta_{m,n-2} + (2n+1)\,\delta_{m,n} - \sqrt{(n+1)(n+2)}\,\delta_{m,n+2}\right] \quad . \tag{4.6}$$

Clearly, these matrix elements vanish unless m and n have the same parity. To calculate $n(E) = n(o,E)$, we can restrict ourselves to the subspace of even functions only. We have taken $\omega = 1$, and numerically diagonalized the matrix (4.6) for two cases. In the first case we used 5 functions and in the second 10. From this we have calculated $n_N(E)$ and $\mathfrak{N}_N(E)$, using Eqs. (3.2) and (3.3). Figures 1a and 1b compare the results with the exact $\mathfrak{N}(E)$, Eq. (4.3). Also shown in these figures are the midpoints of each vertical rise in the approximate integrated density of states. As can be seen, the agreement is very good up to $E \approx 6$ for $N = 5$ and up to $E \approx 15$ for $N = 10$. (In this case the energies scale as ω.) In the Appendix, we prove that as N becomes large, the eigenvalues E^ν become dense, and the approximate integrated density of states converges to the exact result, Eq. (4.3).

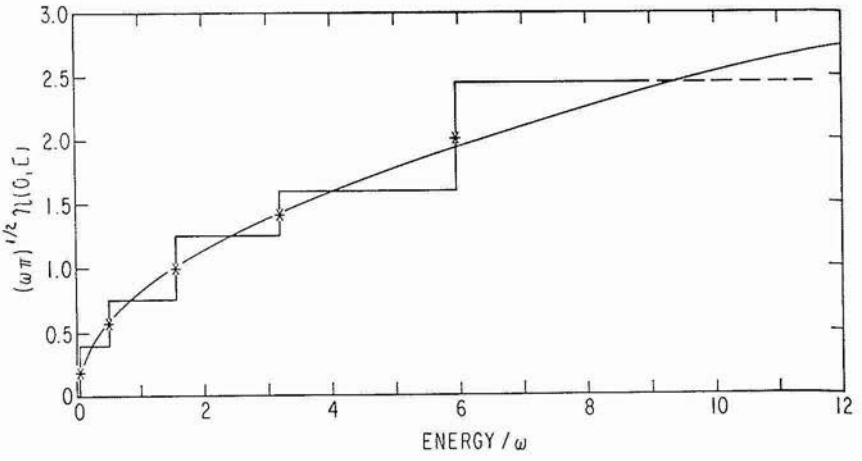
V. SURFACES AND INTERFACES IN A LOCALIZED REPRESENTATION

As a second example of the application of our procedure, we derive the density distribution of the so-called sine-gas, near a surface created by an infinite potential barrier at $x = 0$. We assume the electron gas to occupy the half-space $x \geq 0$. To solve this problem within our formalism, one needs a localized basis near $\mathbf{r} = 0$, which also vanishes at $x = 0$. Two possible bases that fulfill these requirements are for example

$$\psi_{lmn}(\mathbf{r}) = \sqrt{2}\, u_l(z)\, u_m(y)\, u_{2n-1}(x) \tag{5.1}$$

and

$$\tilde{\psi}_{lmn}(\mathbf{r}) = \left(\frac{2l!\,\omega^{m+1}}{(l+m)!\,\pi}\right)^{1/2} e^{im\phi}\, \varrho^m\, e^{-\frac{1}{2}\omega\varrho^2}\, L_l^m(\omega\varrho^2)\, u_{2n-1}(x) \quad , \tag{5.2}$$



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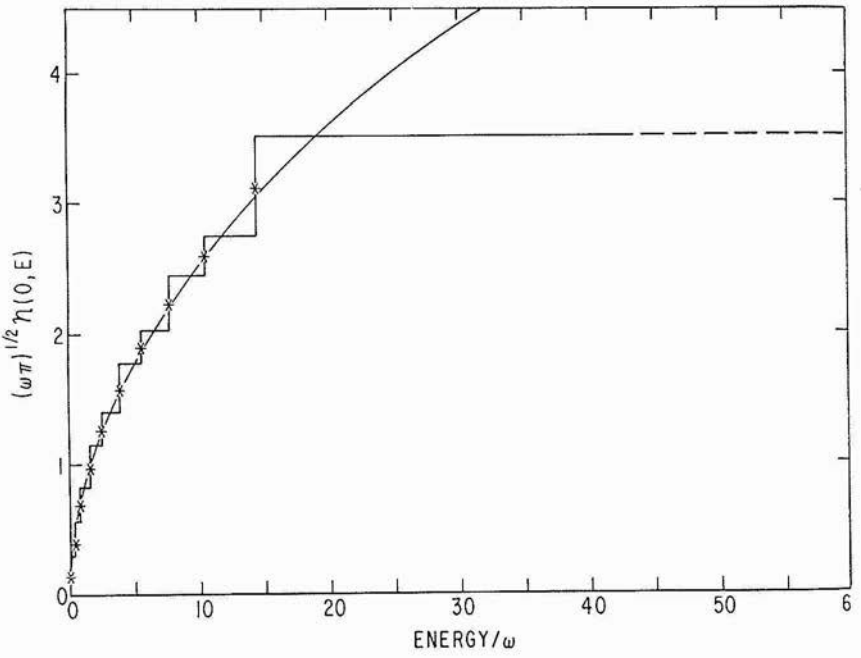

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FIG. 1. A COMPARISON OF THE APPROXIMATE FREE-ELECTRON DENSITY OF STATES (the staircase curve) with the exact result (the smooth curve). (1a) using 5 even oscillator functions, (1b) using 10 even oscillator functions.

where u_n and L_l^m are the harmonic oscillator wave-functions and the associated Laguerre polynomials respectively. The first basis, (5.1), is convenient for problems having cubic symmetry, whereas (5.2) is more suitable for problems with cylindrical symmetry. For the sine-gas, both (5.1) and (5.2) can be used. Since the problem under consideration has translational symmetry parallel to the surface, it is enough to calculate the density distribution for $y=z=0$. Thus, we can further simplify the problem by using only even l and m when using the basis (5.1), or set $m=0$ when using (5.2). Figures 2a and 2b show the density profile near the surface, calculated in both bases, (5.1) and (5.2). Figure 2a shows the result of a calculation done with a set of $10\times10\times10$ functions in the x, y, and z directions, respectively. Figure 2b shows a similar result obtained by using 20 cylindrical functions and 10 functions in the x direction (using the basis (5.2)). As can be seen from these figures, the accuracy of the calculation is quite good near the surface, where the basis functions are localized, and becomes less and less satisfactory as one goes further from the surface.

Our next example is a simple model of a bimetallic interface. This is a free electron gas, moving in a potential field having the form of a step function. The position of the step is the position of the interface, whereas

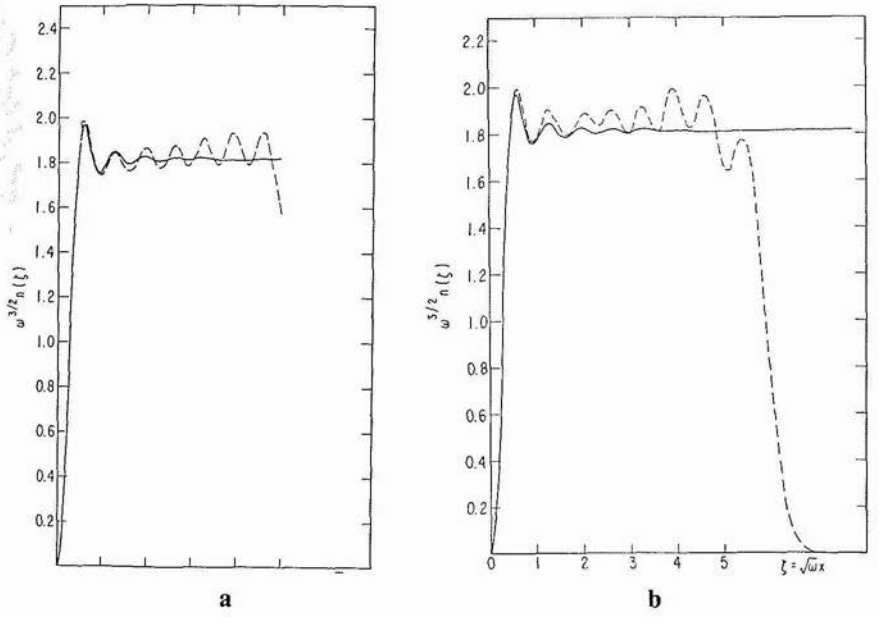

FIG. 2. THE DENSITY PROFILE NEAR THE SURFACE OF A SINE-GAS (solid line), having a Fermi energy of 11.3 ω. The approximate density profile is shown by a dashed line. (2a) is the result obtained by using $10\times10\times10$ functions—see Eq. (5.1). (2b) was obtained by using 20 cylindrical and 10 perpendicular functions.

the step height is equal to the difference between the Fermi levels of the two metals. Figures 3a and 3b show the density profile near such an interface formed by two metals whose Fermi energies differ by 5 eV and whose bulk electron density ratio is equal to 2. The localized basis used to solve this problem is given by

$$\psi_{l,n}(\mathbf{r}) = \left(\frac{\omega}{\pi}\right)^{1/2} e^{-\frac{1}{2}\omega\varrho^2} L_l(\omega\varrho^2)\, u_n(x) \quad , \tag{5.3}$$

which is localized at the interface. Figure 3a shows the result obtained by using 20 functions in the direction perpendicular to the interface, and 20 cylindrical functions parallel to the interface. Figure 3b shows the results of a similar calculation, obtained by using 40 functions in the perpendicular direction and 20 cylindrical functions. Here again, the accuracy of the calculation is best near the localization center, the interface in this case, and becomes worse away from that point.

VI. *s-d* HYBRIDIZATION IN A LOCALIZED REPRESENTATION

Our last example is the application of a localized basis to the problem of *s-d* hybridization in copper along the [100] direction. In choosing the parameters of our model we follow the work of Mueller[10] on the combined interpolation scheme for copper. Along the [100] direction we have effectively a 1-dimensional problem, with a lattice spacing equal to $a = \frac{1}{2}a_o$ where a_o is the cubic parameter of f.c.c. copper, i.e., $a = 1.81$ Å. Since the five *d*-bands do not mix in this symmetry direction, it is sufficient to consider the hybridization of one *d*-band at a time. We describe the *d*-band before hybridization as a tight-binding band, arising from Wannier functions, ϕ_n, localized at the various lattice sites Z_n, and having the symmetry $(3z^2 - \mathbf{r}^2)$. The Bloch functions and energies of this band are given, respectively, by

$$\psi_d = N^{-1/2} \sum_n e^{ikZ_n} \phi_n \tag{6.1}$$

$$E_d(k) = E_o + 2T\cos(ka) \quad , \tag{6.2}$$

where N is the number of atoms in the 1-dimensional problem, and E_o and T are the self-energy and the transfer integral, respectively. Using the same Koster-Slater parameters as those used by Mueller, we obtain $T = 0.386$ eV.

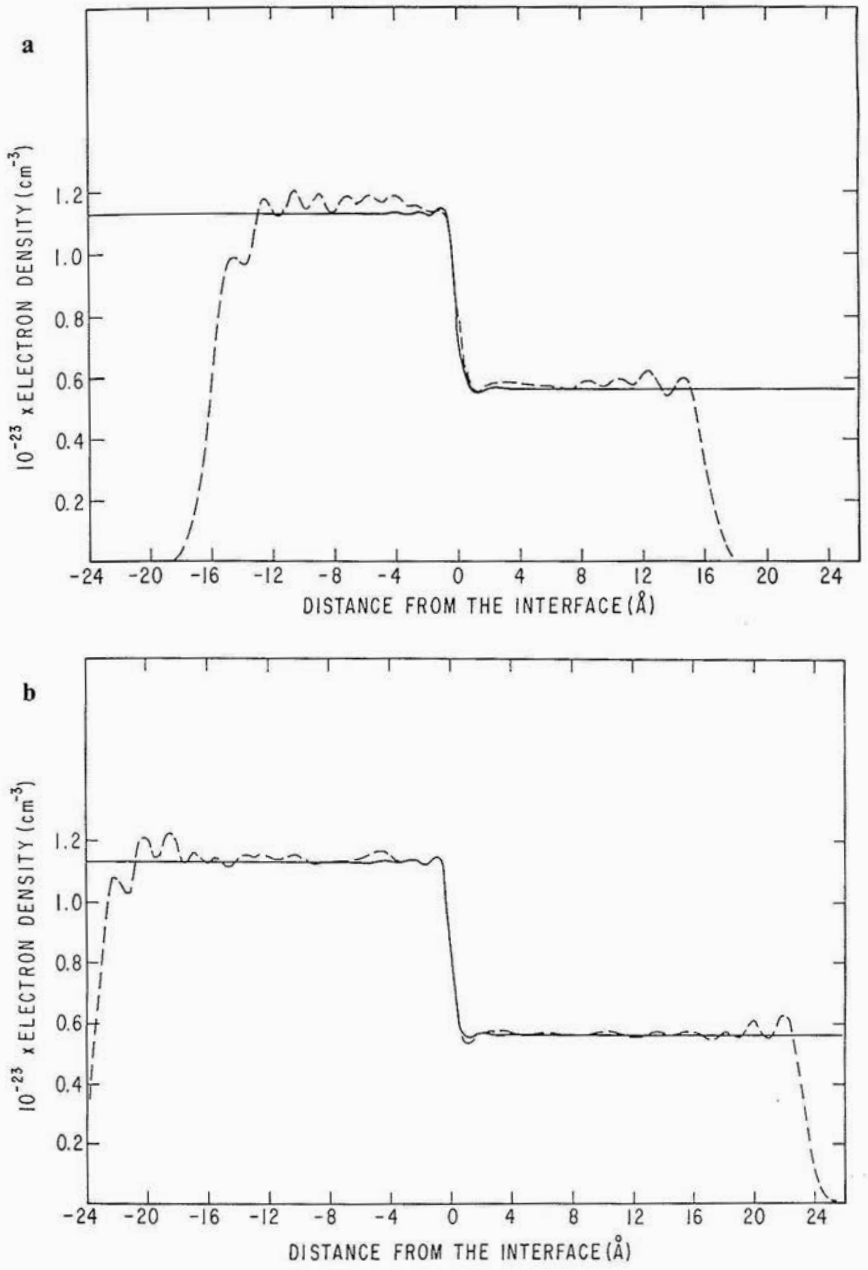

FIG. 3. THE EXACT (solid line) AND THE APPROXIMATE (dashed line) DENSITY DISTRIBUTION near a bimetallic interface. The result of (3a) was obtained by using 20 cylindrical and 20 perpendicular functions, (3b) was obtained by using 20×40 functions.

For E_o we take the actual difference between the bottom of the d-band and the conduction band, i.e., $E_o = 4.67$ eV. Thus, the d-electron energy band is given by

$$E_d(k) = 4.67 + 0.772 \cos(ka) \quad \text{(eV)} \quad . \tag{6.3}$$

For the s-electron wave functions and energies, we use plane waves with an effective mass equal to the copper effective mass in the [100] direction,

$$\psi_\nu = (Na)^{-1/2} e^{i(k+K_\nu)z} \tag{6.4}$$

$$E_\nu(k) = 1.154\,[a(k+K_\nu)]^2 \quad \text{(eV)} \quad , \tag{6.5}$$

where K_ν are the vectors of the reciprocal lattice. We assume that the plane waves (6.4) are orthogonal to the Wannier functions ϕ_n.

For the hybridization term, which couples the s and d electrons, we write

$$g_\nu(k) = \gamma\{\exp(-\alpha[a(k+K_\nu)]^2) - \exp(-\beta[a(k+K_\nu)]^2)\} \tag{6.6}$$

where the parameters α, β, and γ are chosen to simulate Mueller's hybridization function. The coefficient α determines the effective range of $g_\nu(k)$ in k-space. By taking $\alpha = 1.2665 \cdot 10^{-2}$ we obtain a range similar to that of Mueller's. To determine β we require $g(k)$ to have its maximum at the Brillouin zone boundary. This gives $\beta = 0.3485$. For γ we take $\gamma = 1.98$ eV so that $g(k)$ is equal to half the hybridization gap at the crossover point of the s and the d bands before hybridization. To summarize, the Hamiltonian of the hybridized bands is given by

$$(\psi_d|H|\psi_d) = E_d(k) \quad , \tag{6.7.a}$$

$$(\psi_\nu|H|\psi_\nu) = E_\nu(k) \quad , \tag{6.7.b}$$

$$(\psi_\nu|H|\psi_d) = (\psi_d|H|\psi_\nu) = g_\nu(k) \quad . \tag{6.7.c}$$

The band structure of this Hamiltonian, obtained by a numerical diagonalization of the matrix (6.7) for various values of k, is shown in figure 4.

Let $\psi^\alpha(k)$ be the Bloch function of the α hybridized band. This wave function can be written as a linear combination of the non-hybridized wave functions

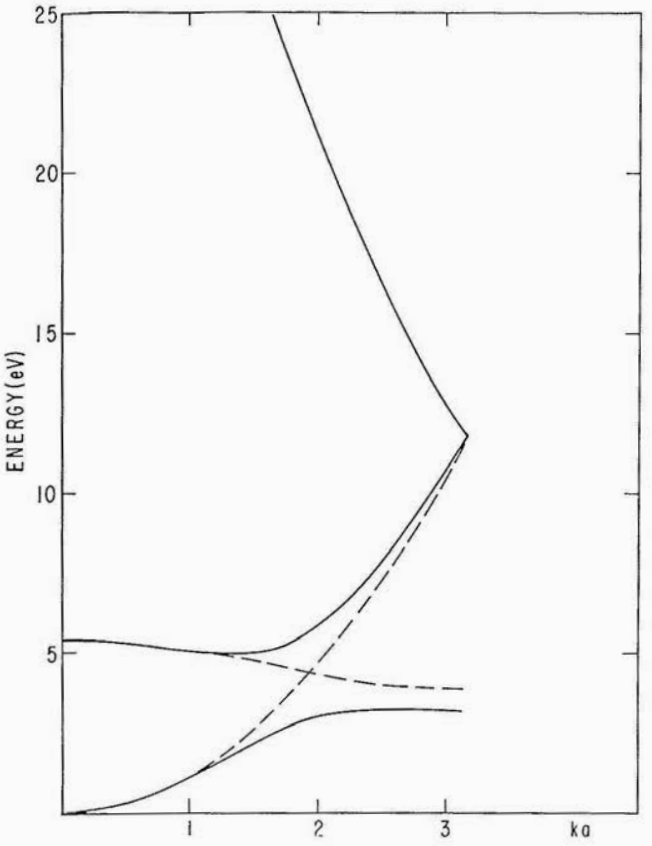

FIG. 4. THE BAND STRUCTURE OF THE HYBRIDIZED COPPER HAMILTONIAN. Shown by a dashed line is the band structure before hybridization.

$$\psi^{\alpha}(k) = c^{\alpha}(k)\psi_d + \sum_{\nu} a_{\nu}^{\alpha}(k)\psi_{\nu} \quad , \tag{6.8}$$

where c^{α} and a_{ν}^{α} are the corresponding expansion coefficients. From the equation above we can define the d density of states per atom as

$$n_d(E) = N^{-1} \sum_{\alpha,k} |c^{\alpha}(k)|^2 \delta(E - E^{\alpha}(k))$$

$$= \frac{a}{\pi} \sum_{\alpha} \frac{|c^{\alpha}(k)|^2}{|dE^{\alpha}(k)/dk|}\Bigg|_{E^{\alpha}(k)=E} \quad , \tag{6.9}$$

where $E^{\alpha}(k)$ is the energy of the α hybridized band. The corresponding integrated density of states is given by

$$\mathcal{N}_d(E) = \int_{-\infty}^{E} n_d(E')dE' = \frac{a}{\pi}\sum_{\alpha}\int_{0}^{\pi/a} |c^{\alpha}(k)|^2\theta(E-E^{\alpha}(k))dk, \quad (6.10)$$

where θ is the unit step function.

In a similar way we can also define the local s-density of states, and the corresponding integrated density, by

$$n_s(z,E) = a\sum_{\alpha,k} \Big|\sum_{\nu} a_{\nu}^{\alpha}(k)\psi_{\nu}(z)\Big|^2\delta(E-E^{\alpha}(k))$$

$$= \frac{a}{\pi}\sum_{\alpha,\mu,\nu}\frac{a_{\nu}^{\alpha}(k)\,a_{\nu}^{\alpha}(k)^*}{|dE^{\alpha}(k)/dk|}e^{i(K_{\nu}-K_{\mu})z}\Bigg|_{E^{\alpha}(k)=E} \quad (6.11)$$

and

$$\mathcal{N}_s(z,E) = \quad (6.12)$$

$$\frac{a}{\pi}\sum_{\alpha,\mu,\nu}\int_{0}^{\pi/a} a_{\nu}^{\alpha}(k)\,a_{\mu}^{\alpha}(k)^*e^{i(K_{\nu}-K_{\mu})z}\theta(E-E^{\alpha}(k))dk \quad .$$

To solve the hybridization model in a localized basis, we use the Wannier functions $\{\phi_n\}$ and the harmonic oscillator functions $\{u_{\nu}\}$. We assume that the set $\{u_{\nu}\}$ is orthogonal to $\{\phi_n\}$ (as was the set of plane waves $\{\psi_{\nu}\}$). In this basis, the hybridized Hamiltonian is given by

$$(\phi_n|H|\phi_n) = E_o \quad ,$$

$$(\phi_n|H|\phi_{n\pm1}) = T \quad ,$$

$$(u_{\nu}|H|u_{\mu}) = \frac{\hbar^2\omega}{4m^*}\Big[-\sqrt{\mu(\mu-1)}\,\delta_{\nu,\mu-2} + (2\mu+1)\delta_{\mu,\nu}$$

$$-\sqrt{(\mu+1)(\mu+2)}\,\delta_{\nu,\mu+2}\Big] \quad ,$$

$$(u_{2\nu}|H|\phi_n) = a^{1/2}\gamma\left[\frac{1}{(1+2\alpha a^2\omega)^{1/2}}\left(\frac{1-2\alpha a^2\omega}{1+2\alpha a^2\omega}\right)^{\nu}\right.$$

$$\exp\left(\frac{\alpha a^2\omega^2 Z_n^2}{1-4\alpha^2 a^4\omega^2}\right)\times u_{2\nu}\left(Z_n\sqrt{\frac{\omega}{1-4\alpha^2 a^4\omega^2}}\right)$$

$$-\frac{1}{(1+2\beta a^2\omega)^{1/2}}\left(\frac{1-2\beta a^2\omega}{1+2\beta a^2\omega}\right)^{\nu}\exp\left(\frac{\beta a^2\omega^2 Z_n^2}{1-4\beta^2 a^4\omega^2}\right)\times$$

$$\left.u_{2\nu}\left(Z_n\sqrt{\frac{\omega}{1-4\beta^2 a^4\omega^2}}\right)\right],$$

$$(u_{2\nu+1}|H|\phi_n) = a^{1/2}\gamma\left[\frac{1}{(1+2\alpha a^2\omega)^{1/2}}\left(\frac{1-2\alpha a^2\omega}{1+2\alpha a^2\omega}\right)^{\nu+1/2}\right.$$

$$\exp\left(\frac{\alpha a^2\omega^2 Z_n^2}{1-4\alpha^2 a^4\omega^2}\right)\times u_{2\nu+1}\left(Z_n\sqrt{\frac{\omega}{1-4\alpha^2 a^4\omega^2}}\right)$$

$$-\frac{1}{(1+2\beta a^2\omega)^{1/2}}\left(\frac{1-2\beta a^2\omega}{1+2\beta a^2\omega}\right)^{\nu+1/2}\exp\left(\frac{\beta a^2\omega^2 Z_n^2}{1-4\beta^2 a^4\omega^2}\right)\times \tag{6.13}$$

$$\left.u_{2\nu+1}\left(Z_n\sqrt{\frac{\omega}{1-4\beta^2 a^4\omega^2}}\right)\right],$$

where $Z_n = na$, $n = 0, \pm 1, \pm 2, \ldots$ are the lattice sites, and ω is the frequency of the oscillator. For the present calculation we have taken $\omega = a^{-2}$. For practical purposes we have also taken a finite linear chain, with an odd number of atoms, and calculated the density of states at the central atom. Figure 5 shows the integrated d density of state, whereas figure 6 shows the corresponding integrated s local density of states at the origin. Both calculations were done with a chain of 41 atoms and using 40 harmonic oscillator functions. As can be seen from these figures, the agreement with the exact results is quite good.

VII. DISCUSSION

In this paper we have shown how local electronic structure in an ex-

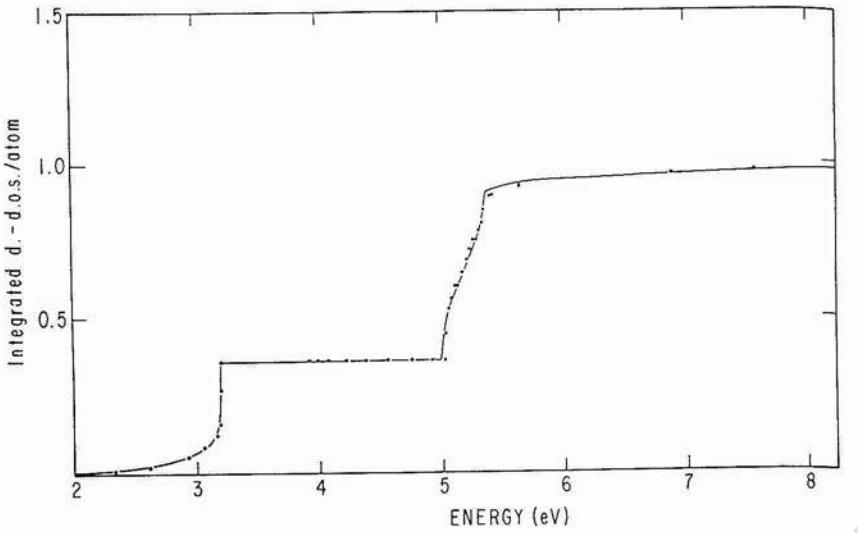

FIG. 5. THE INTEGRATED *d*-DENSITY OF STATES. The points • were obtained using a chain of 41 atoms and 40 oscillator functions.

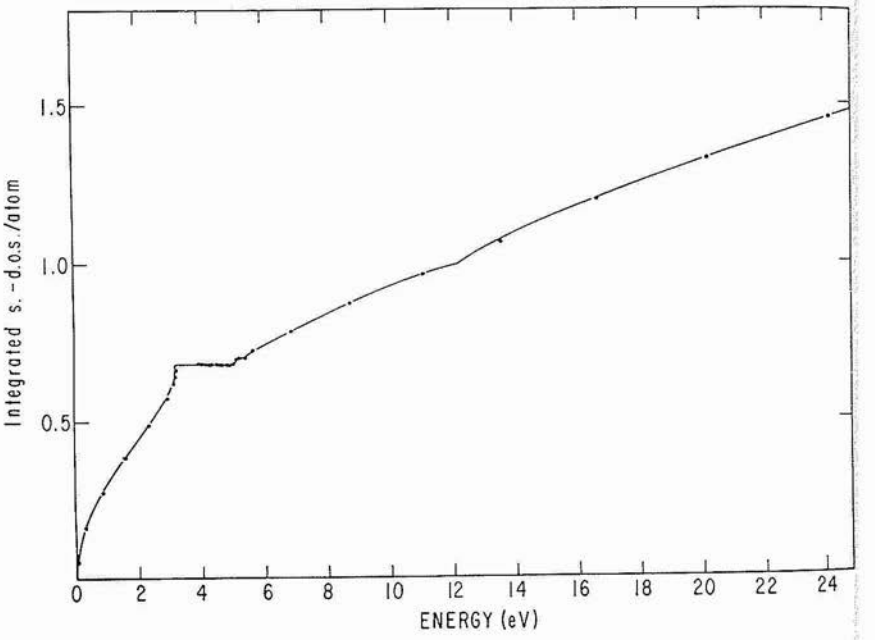

FIG. 6. THE INTEGRATED *s*-DENSITY OF STATES AT A LATTICE SITE. The points • were obtained using the same approximation as in figure 5.

tended system can be calculated in a basis of localized functions, even when the actual eigenfunctions are delocalized. In particular, given any effective potential $V_{\text{eff}}(\mathbf{r})$, the total electron density, $n(\mathbf{r})$, can be obtained by integration of $n(\mathbf{r},E)$ over E. In this way, the method can be naturally integrated into the density functional formalism,[8,9] which includes many-body effects.

This method would seem to be especially appropriate for localized defects, such as the surface and interface systems treated in section V, even for hybridized wavefunctions, such as those discussed in section VI. A successful self-consistent calculation for a vacancy, using our method, has been carried out by F. Perrot.[11] Other possible applications are local portions of large molecules.

APPENDIX

In this Appendix we prove the convergence of the procedure of section IV for the one-dimensional free electron gas. To this end we shall calculate explicitly the eigenvectors and the eigenvalues of the truncated Hamiltonian (Eq. (4.6)) in the harmonic oscillator basis. We shall show that as the size of the Hamiltonian matrix is increased, the eigenvalues become dense, and the integrated approximate local density of states, evaluated by using Eq. (3.3), approaches the exact result.

The free electron Hamiltonian has the representation (4.6) in the harmonic oscillator basis. We now approximate this Hamiltonian by a finite matrix of order $2N\times 2N$, whose matrix elements are given by (4.6) with $m,n=0,1\ldots 2N-1$. This Hamiltonian can be written as a direct sum of two tridiagonal matrices by separating the even and the odd functions. In this way we have

$$H_o = H_o^- + H_o^+ \quad , \tag{A.1}$$

where H_o^- and H_o^+ are the corresponding representations of H_o in the even and the odd subspaces, respectively. Thus, the problem of diagonalizing the $2N\times 2N$ matrix (4.6) can be separated into two independent problems of diagonalizing the smaller two $N\times N$ matrices $H_o^{\mp}$. Using Eq. (4.6), these matrices are given explicitly by

$$(m|H_o^-|n) \equiv (2m|H_o|2n) =$$

$$\frac{\omega}{4}\left[-\sqrt{(2n-1)2n}\,\delta_{m,n+1} + (4n+1)\delta_{m,n} - \sqrt{(2n+1)(2n+2)}\delta_{m,n+1}\right]$$

$$m,n = 0,1,\ldots N-1 \quad ; \tag{A.2}$$

$$(m|H_o^+|n) \equiv (2m-1|H_o|2n-1) =$$

$$\frac{\omega}{4}\left[-\sqrt{(2n-2)(2n-1)}\delta_{m,n+1} + (4n-1)\delta_{m,n} - \sqrt{2n(2n+1)}\delta_{m,n+1}\right]$$

$$m, n = 1, 2, \ldots N \quad . \tag{A.3}$$

It is well known that the characteristic equation of a symmetric tridiagonal matrix can be generated by a recursion relation.[12] In this way, the leading principal minors, of order n, $B_n^{\mp}(y)$ of the matrix $H_o^{\mp} - yI$, obey the recursion relation

$$B_{n+1}^{\mp}(y) = (4n+2\mp 1-y)B_n^{\mp}(y) - 2n(2n\mp 1)B_{n-1}^{\mp}(y)$$

$$B_o^{\mp}(y) = 1$$

$$B_{-1}^{\mp}(y) = 0 \tag{A.4}$$

where y is the dimensionless energy variable,

$$y = 4E/\omega \quad . \tag{A.5}$$

By comparing the recursion relation (A.4) to the recursion relation obeyed by the associated Laguerre polynomials, one can verify that the polynomials $B_n^{\mp}(y)$ are related to the well known polynomials $L_n^{\mp 1/2}(y)$. In fact we have

$$B_n^{\mp}(y) = 2^n n!\, L_n^{\mp 1/2}(y/2) \quad . \tag{A.6}$$

Using the relation between $L_n^{\mp 1/2}$ and the Hermite polynomials we can also write

$$B_n^{-}(y) = \frac{(-1)^n}{2^n} H_{2n}(\sqrt{y/2}) \quad , \tag{A.7}$$

$$B_n^{+}(y) = \frac{(-1)^n}{2^{n+1}\sqrt{y/2}} H_{2n+1}(\sqrt{y/2}) \quad . \tag{A.8}$$

The eigenvalues of the truncated Hamiltonian are given by the roots of $B_N^{\mp}(y)$. As can be seen from Eqs. (A.7) and (A.8), these eigenvalues are simply related to the positive roots of the Hermite polynomials of order $2N$

and $2N+1$. For large N we can use the asymptotic expression[13] for the Hermite polynomials to obtain

$$y_\nu^- = \frac{2\pi^2(\nu-\tfrac{1}{2})^2}{4N+1} + 0\,(N^{-3/2}) \quad , \tag{A.9}$$

$$y_\nu^+ = \frac{2\pi^2\nu^2}{4N+3} + 0\,(N^{-3/2}) \quad , \tag{A.10}$$

where $y_\nu^{\mp}$ are the corresponding eigenvalues. As can be seen from these equations, the eigenvalues $y_\nu^{\mp}$ become dense on the positive y_ν axis as the value of N is increased. In fact, we have

$$y_\nu - y_{\nu-1} \sim \pi\left(\frac{2\,y_\nu}{N}\right)^{1/2} \quad . \tag{A.11}$$

We turn now to the determination of the eigenvectors of the approximate Hamiltonian. Since the matrices $H_o^{\mp}$ are tridiagonal, the unnormalized eigenvectors, corresponding to the eigenvalue y_ν, can be written explicitly.[12] Using the expressions derived for $B_n^{\mp}(y)$ and the expression for the off-diagonal matrix elements of $H_o^{\mp}$, we obtain

$$c_m^{-\nu} = \frac{(-1)^m}{2^m\sqrt{2m!}}\,H_{2m}(\sqrt{y_\nu^-/2})$$

$$m = 0,1,\ldots \qquad N-1 \tag{A.12}$$

and

$$c_m^{+\nu} = \frac{(-1)^{m-1}}{2^m}\left(\frac{2}{(2m-1)!\,y_\nu^+}\right)^{1/2} H_{2m-1}(\sqrt{y_\nu^+/2})$$

$$m = 1,2,\ldots \qquad N \quad . \tag{A.13}$$

In order to normalize the eigenvectors we have to evaluate the following sums:

$$N_\nu^- = \sum_{m=0}^{N-1}(c_m^{-\nu})^2 = \sum_{m=0}^{N-1}\frac{H_{2m-1}^2\,(\sqrt{y_\nu^-/2})}{2^{2m}(2m)!} \tag{A.14}$$

and

$$N_\nu^+ = \sum_{m=1}^{N} (c_m^{+\nu})^2 = \frac{1}{y_n^+} \sum_{m=1}^{N} \frac{H_{2m-1}^2(\sqrt{y_\nu^+/2})}{2^{2m-1}(2m-1)!} \quad . \tag{A.15}$$

By using the corresponding recursion relations, one can show that any family of orthonormal polynomials, $\{P_n(x)\}$ with respect to a symmetric weight function, obey the following summation identities:

$$\sum_{m=0}^{n} P_{2m}^2(x) = \frac{P'_{2n+2}(x)\,P_{2n}(x) - P'_{2n}(x)\,P_{2n+2}(x)}{2\,A_{2m+2}x} \tag{A.16}$$

$$\sum_{m=1}^{n} P_{2m-1}^2(x) = \frac{P'_{2n+1}(x)\,P_{2n-1}(x) - P'_{2n-1}(x)\,P_{2n+1}(x)}{2\,A_{2m+1}x} \tag{A.17}$$

where

$$A_n = k_n/k_{n-2} \quad , \tag{A.18}$$

and k_n is the coefficient of x^n in $P_n(x)$. Using these identities in the case of the Hermite polynomials gives, after several manipulations,

$$N_\nu^- = \frac{N}{2^{2N-1}(2N-1)!} H_{2N-1}^2(\sqrt{y_\nu^-/2}) \quad , \tag{A.19}$$

$$N_\nu^+ = \frac{(2N+1)}{(y_\nu^+/2)\,2^{2N+2}(2N)!} H_{2N}^2(\sqrt{y_\nu^+/2}) \quad . \tag{A.20}$$

For large N we can use the asymptotic behavior of the Hermite polynomials to obtain

$$N_\nu^- \sim \left(\frac{N}{\pi}\right)^{1/2} \exp(y_\nu^-/2) \tag{A.21}$$

$$N_\nu^+ \sim \left(\frac{N}{\pi}\right)^{1/2} \frac{\exp(y_\nu^+/2)}{y_\nu^+} \tag{A.22}$$

To complete our proof, we evaluate now the residue associated with the various eigenvalues $R_\nu^{\pm}(x)$, which gives the corresponding jump in the in-

tegrated local density of states. Using Eqs. (A.12)-(A.13) and (A.19)-(A.20), we can write

$$R_\nu^-(x) = (N_\nu^-)^{-1} \left[\sum_{m=0}^{N-1} c_m^{-\nu} u_{2n}(x) \right]^2$$

$$= \frac{\pi^{1/2} e^{y_\nu^-/2}}{N_\nu^-} \left[\sum_{m=0}^{N-1} (-1)^m u_{2m}(x)\, u_{2m}(\sqrt{y_\nu^-/2}) \right]^2 , \quad \text{(A.23)}$$

$$R_\nu^+(x) = (N_\nu^+)^{-1} \left[\sum_{m=1}^{N} c_m^{+\nu} u_{2m-1}(x) \right]^2$$

$$= \frac{\pi^{1/2} e^{y_\nu^+/2}}{N_\nu^+ y_\nu^+} \left[\sum_{m=1}^{N} (-1)^m u_{2m-1}(x)\, u_{2m-1}(\sqrt{y_\nu^+/2}) \right]^2 , \quad \text{(A.24)}$$

where $u_n(x)$ are the normalized harmonic oscillator wavefunctions.

It is not difficult to show that the sums that appear in Eqs. (A.23) and (A.24) above are related to the cosine and sine functions, respectively. In fact, for large N we have

$$\sum_{m=0}^{N-1} (-1)^m u_{2m}(x)\, u_{2m}(\sqrt{y_\nu^-/2}) = \frac{\cos(x\sqrt{y_\nu^-/2})}{(2\pi)^{1/2}} + 0(N^{-1/2}) , \quad \text{(A.25)}$$

$$\sum_{m=1}^{N} (-1)^m u_{2m-1}(x)\, u_{2m-1}(\sqrt{y_\nu^+/2}) = \frac{\sin(x\sqrt{y_\nu^+/2})}{(2\pi)^{1/2}} + 0(N^{-1/2}) . \quad \text{(A.26)}$$

Applying the asymptotic expressions (A.21)-(A.22) for $N_\nu^\mp$, the residues $R_\nu^\mp(x)$ are given, for large N, by

$$R_\nu^-(x) \sim \frac{\cos^2(x\sqrt{y_\nu^-/2})}{2N^{1/2}} , \quad \text{(A.27)}$$

$$R_\nu^+(x) \sim \frac{\sin^2(x\sqrt{y_\nu^+/2})}{2N^{1/2}} . \quad \text{(A.28)}$$

But from Eqs. (A.9) and (A.10)

$$\cos^2(x\sqrt{y_\nu^-/2}) + \sin^2(x\sqrt{y_\nu^+/2}) = 1 + 0(N^{-1}) \quad ,$$

and therefore, for large N

$$R_\nu^-(x) + R_\nu^+(x) \sim \frac{1}{2N^{1/2}} \quad . \tag{A.29}$$

The approximate integrated local density of states is given by Eq. (3.3). Thus, for large N we obtain from (A.29)

$$\begin{aligned} \mathfrak{N}_N(x,E) &= \sum_{E^\nu \le E} [R_\nu^-(x) + R_\nu^+(x)] \\ &= \frac{\nu_{\max}}{2N^{1/2}} \quad , \end{aligned} \tag{A.30}$$

where $\nu_{\max}$ is defined by

$$E^{\nu_{\max}} = E$$

From Eqs. (A.9)-(A.10) $\nu_{\max}$ is given by

$$\nu_{\max} = 2(2EN)^{1/2}/\pi \quad . \tag{A.31}$$

Substituting this expression into Eq. (A.30) gives

$$\mathfrak{N}_N(x,E) = (2E)^{1/2}/\pi \quad . \tag{A.32}$$

for large N, which is identical with the exact expression for $\mathfrak{N}(x,E)$, Eq. (4.3).

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